Effect of Pressure on Pyrolysis of a Sub-bituminous Coal in an Entrained-Flow Reactor

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Introduction

To help produce advances in gasification technologies it is necessary to generate data on the effect of coal properties and operating variables on the pyrolysis/gasification behavior of coals under conditions similar to those in advanced-concept gasifiers; usually a high temperature-high pressure environment for entrained coal particles. Since relatively little data are available on coal pyrolysis/gasification at elevated pressure, especially in entrained flow systems, the primary objective of this study was to provide information on the effect of pressure on product yield and composition during pyrolysis.

The thermal decomposition of coal produces solid char or coke plus liquid and gaseous volatile matter (1):

$$\text{coal} \xrightarrow{\text{heat}} \text{solid (char or coke)} + \text{liquid (tar)} + \text{gas } (CO, CO_2, CH_4, \text{etc})$$

The char consists mainly of carbon along with small amounts of hydrogen, oxygen, nitrogen and sulfur as well as the ash produced from the mineral matter. Tars are vapors at the pyrolysis temperature and pressure. The quality and quantity of char, tar and gases produced during pyrolysis depend on coal type, temperature, heating rate, pressure, residence time and particle size (1).

Two general techniques have been used for coal pyrolysis studies (2): captive sample, where the coal is stationary or fixed during a run, and entrained-flow, where the coal is fed and products withdrawn continuously. Most data on pressure effects have been obtained using captive sample techniques (3-9). For example, Anthony et al. found a substantial reduction in weight loss with increasing pressure for the pyrolysis of a bituminous coal above 873 K (4). Suuberg et al. also reported a reduction in weight loss and tar yield with increasing pressure (7).

The entrained-flow technique, however, has been used more in recent years by researchers (10-16). Sundaram et al. examined the effect of pressure on pyrolysis of a sub-bituminous coal under various inert gas pressures (Ar, He and N_2) in an entrained-flow reactor (12). They reported that the tar yield increased with increasing pressure of helium, while it decreased with increasing pressure of argon. They also reported that the total carbon conversion went through a maximum before decreasing with increasing pressure. Serio et al., on the other hand, reported a reduction of about 25% in tar yield with increasing pressure for four different coals(13). A study similar to the one reported here on Montana Rosebud coal under the same pressure conditions but at higher temperatures and residence times has also been reported by Bissett (14).

Experimental

An entrained-flow reactor, which was capable of subjecting pulverized coal particles to temperatures and pressures of 1373°K and 1000 psig respectively for a range of particle residence times was used in this study. The reactor, which is equipped with a computerized data acquisition system for accurate monitoring of the experimental conditions, is shown schematically in Figure 1. Pulverized coal is injected into the furnace by entrainment in a cold gas stream (primary gas) as it passes through a semi-venturi. The coal laden gas flows through a water-cooled injector probe fixed at the top of the furnace. A secondary gas stream which is preheated during its passage upward through an annular region surrounding the reactor tube enters the furnace near the tip of the injector probe. Char is collected by a water-cooled probe which can be adjusted over a range of distances from the bottom of the furnace. This gives the flexibility to change the pyrolysis residence time. Another method of changing residence times is to adjust the gas flow rates of the gases passing through the furnace.

Char is separated from the product stream in a filter vessel installed downstream of the collector probe. The particle-laden stream enters the cylindrically-shaped vessel tangentially and at a point midway up the vessel. The solid char falls into a sample vessel at the bottom of the cylinder, while much of the tar is trapped by a 20 µm stainless steel filter at the top of the vessel. The solid pyrolysis products and the material trapped by the filter both were extracted in a conventional Soxhlet apparatus using tetrahydrofuran (THF) as the solvent. The THF solubles, which are used to represent the tars produced during pyrolysis, were obtained by evaporating the solvent after extraction. The THF insolubles are used to represent the char yield.

Proximate analyses were performed on the chars using a Leco MAC-400 analyzer. Ultimate analyses were also performed on chars and tars using a Leco CHN-600 analyzer. Sulfur contents were measured by a Leco sulfur analyzer. The gas stream leaving the collector vessel is routed through an on-line Carle gas chromatograph which is capable of monitoring the following gases: H_2, N_2, O_2, H_2S, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, H_2O, SO_2, and $C_3 + C_4$ hydrocarbons. An infrared gas analyzer is used to continuously monitor the carbon monoxide concentration in the outlet gas stream to determine when the reactor has reached steady-state operation. Gas composition measured by the GC is then determined for steady-state pyrolysis. The furnace is operated from a remote control panel and monitored by computer.

Samples of sized Montana Rosebud sub-bituminous coal, with mean particle size of 57µm, were used in this study. Proximate and ultimate analyses of the raw coal are shown in Table 1. Pyrolysis experiments were performed at a temperature of 1189°K, applied N_2 pressures of 100-900 psig and residence times between 0.1 to 1.7 seconds. Coal particle residence times in the furnace were determined by using a computer flow model, which is a modified version of the one developed by Tsai for entrained-flow reactors operated at atmospheric pressure (17). We modified the flow model programs for use under our high-pressure entrained-flow reactor conditions.

Weight loss due to pyrolysis was calculated by using ash as a tracer. On a dry-ash-free basis, the governing equation is:

$$\Delta W = 100\% \left[1 - \frac{A_0\,(100 - A_1)}{A_1\;(100 - A_0)} \right]$$

where ΔW is the calculated weight loss on a daf basis, A_0 is the proximate ash content of the dry coal and A_1 is the proximate ash content of the dry char produced during pyrolysis. An assumption in this calculation is that mineral matter in the coal does not undergo transformations during the pyrolysis which would change the quantity of ash produced upon ashing the chars (15). Tar yields were calculated from the total amount of THF solubles collected, about 5-15%, and expressed as weight percent of coal (daf) fed into the reactor. Total gas yields were calculated from the difference between the weight loss and tar yield.

Results and Discussion

The effect of pressure on weight loss for pyrolysis at 1189°K, 0.3-1.0 seconds residence time and up to 900 psig applied N_2 pressure is shown in Figure 2. It is observed that at short residence times (0.3 and 0.5 seconds) increasing the pressure reduces the weight loss, but at a longer residence time (1.0 seconds) increasing the pressure increases the weight loss slightly after going through a minimum at 178 psig. The weight loss of the Montana Rosebud coal increased steadily with increasing residence time and reached a maximum at 1.0 seconds.

Figure 3 shows the effect of pressure on tar yield at 1189°K, 0.3-1.0 seconds residence time and up to 900 psig applied N_2 pressure. The tar yield increased significantly with pressure up to 178 psig for all residence times and, with the exception of short residence time (0.3 sec) tar, then continued to increase with increasing pressure but at a slower rate. The data are in agreement with those of Solomon et al., who reported similar tar yields for the Montana Rosebud coal at 1089°K and 0.47 seconds residence time (16). The data are also in general agreement with those of Sundaram et al. (12) who reported an increase in tar yield from a sub-bituminous coal with increasing pressure of helium.

Yields and composition of gaseous products are shown in Figures 4 and 5, respectively. Comparison of Figures 2, 3 and 4 indicate that the trend for total gas yield is consistent with the effect of pressure on weight loss and tar yield. The total gas yield drops as the pressure increases from 100 to 178 psig then increases slightly with further increase in pressure. This is also in a good agreement with the data of Solomon et al. At short residence time (0.3 seconds) CO and CO_2 yields increased significantly with increasing N_2 pressure while the CH_4 yield decreased. Reduction in CH_4 yield with increasing pressure has been reported by Serio et al. (13) In the experiments carried out at residence times higher than 0.3 seconds CO concentrations were higher than CO_2, and the concentration of CH_4 was higher than that of C_2H_4 which, in turn, was higher than C_2H_6. This is in good agreement with the data of Sundaram et al. (12) but agrees with that of Serio et al. (13) only for the CH_4, C_2H_4 and C_2H_6 hydrocarbon gases.

The effect of pressure on the C/H ratio of the tar and char produced from pyrolysis is shown graphically in Figure 6 and 7, respectively. It can be seen in Figure 6 that the C/H ratio of the tars remains relatively constant except at short residence times where there is a significant drop in the C/H ratio at 178 psig. Figure 7, on the other hand, shows that the C/H ratio of the char decreases significantly as pressure increases. At short residence times the C/H ratio of the char drops from over 1.8 at 100 psig to below 1.4 at 178 psig then remains relatively constant. At the longer residence time the C/H ratio decreases gradually from over 2.2 at 100 psig to 1.8 at 900 psig N_2 pressure.

Conclusions

Pyrolysis of a Montana Rosebud subbituminous coal in a high pressure entrained flow reactor revealed the following:

1. Based on the weight loss, tar and gas yield, and C/H ratio of the tar and char, it appears that a significant change in pyrolysis behavior occurs at a pressure between 100 and 178 psig.

2. Weight loss and gas yield decrease with increasing pressure up to about 200 psig, and above this pressure there is no significant effect.

3. Tar yield is most affected by the pressure, increasing significantly with increasing pressure up to 200 psig.

4. The maximum tar yield was observed at a low residence time (0.3 seconds) and 178 psig applied N_2 pressure.

5. The CH_4 and C_2H_6 yields decreased significantly with increasing pressure, with C_2H_6 diminishing above 300 psig pressure for a residence time of 1.0 second.

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Table I

Characteristics of Montana Rosebud Subbituminous Coal Used in Pyrolysis Experiments

Proximate Analysis	wt% (dry)
Moisture	—
Volatile Matter	42.7
Ash	9.7
Fixed Carbon (by diff.)	47.6
Ultimate Analysis	**wt% (daf)**
Carbon	74.3
Hydrogen	6.0
Nitrogen	1.0
Sulfur	1.5
Oxygen (by diff.)	17.2

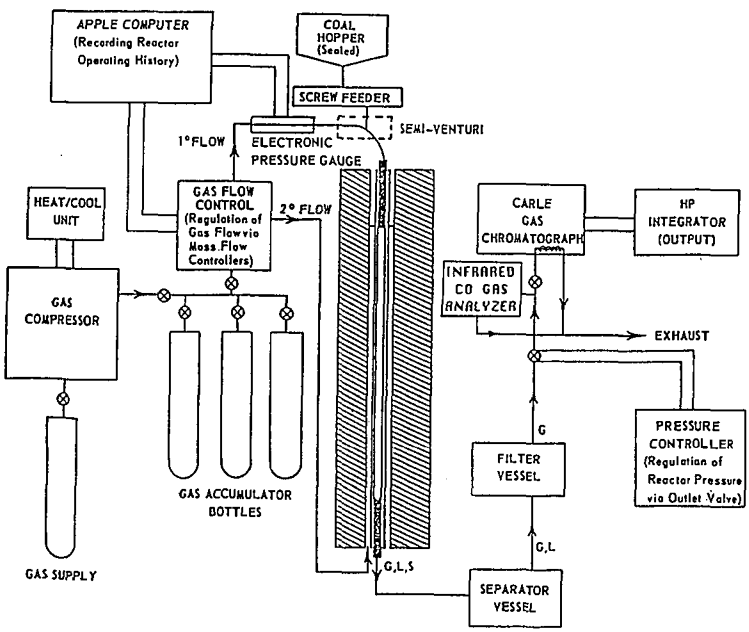

Figure 1. REACTOR CONFIGURATION

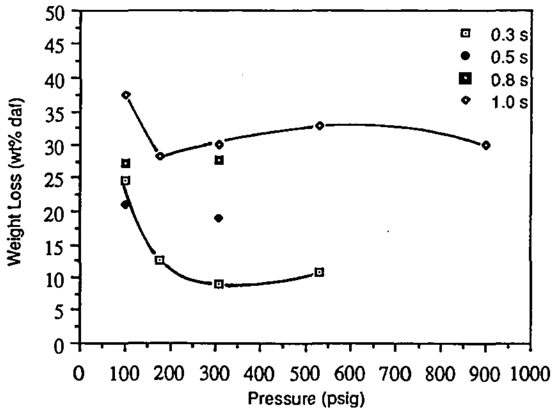

Figure 2. Effect of Pressure on Pyrolysis Weight Loss from Montana Rosebud Coal at 1189 K

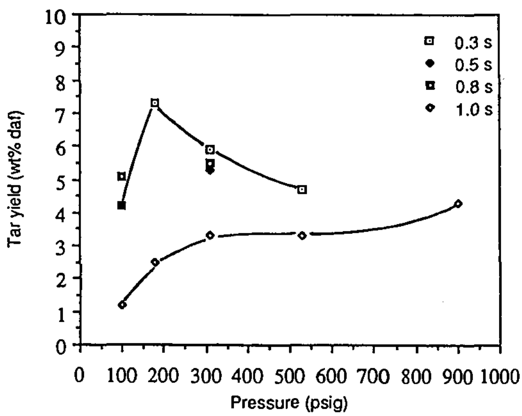

Figure 3. Effect of Pressure on Pyrolysis Tar Yield from Montana Rosebud Coal at 1189 K

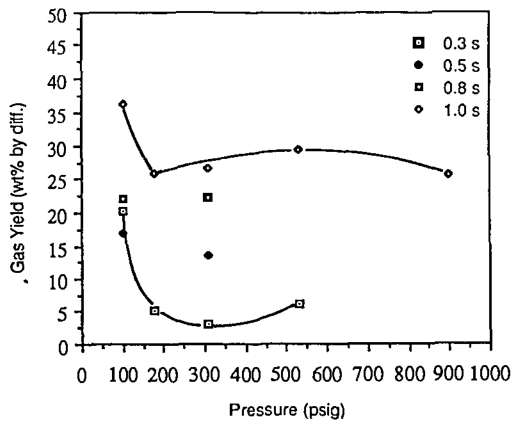

Figure 4. Effect of Pressure on Pyrolysis Gas Yield from Montana Rosebud Coal at 1189 K

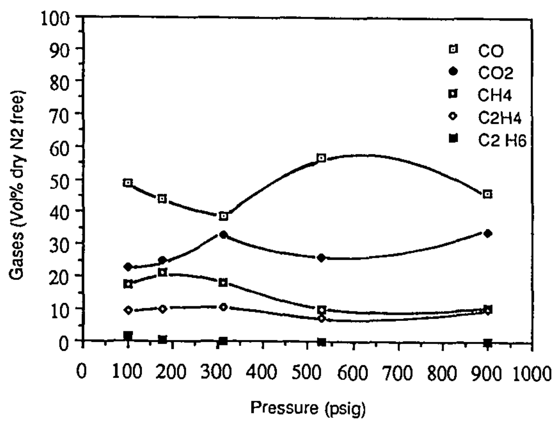

Figure 5. Effect of Pressure on Pyrolysis Gas Composition from Montana Rosebud Coal at 1189 K and 1.0 s

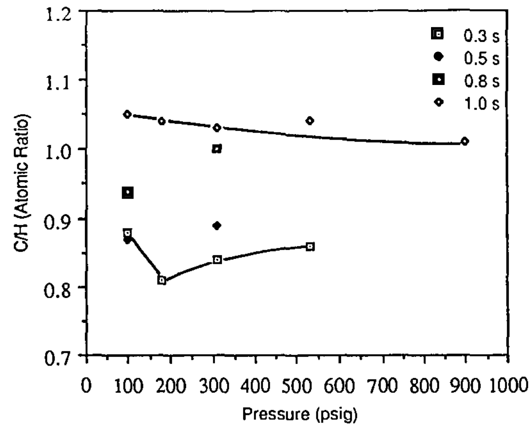

Figure 6. Effect of Pressure on C/H Ratio of Tar from Pyrolysis of Montana Rosebud Coal at 1189 K

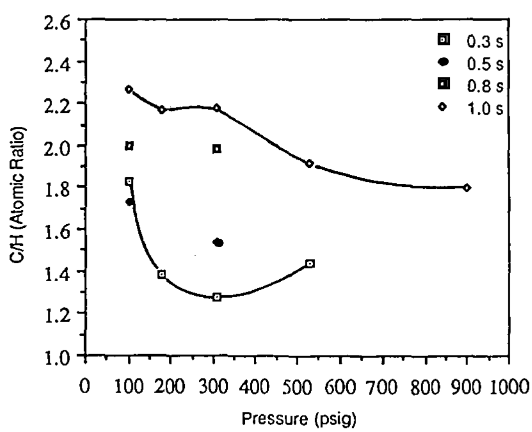

Figure 7. Effect of Pressure on C/H Ratio of Char from Pyrolysis of Montana Rosebud Coal at 1189 K